Effect of mixing ratio of anionic and nonionic emulsifiers on the kinetic behavior of methyl methacrylate emulsion polymerization

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ABSTRACT:

Emulsion polymerization of methyl methacrylate was carried out using a mixture of anionic emulsifier, sodium dodecyl sulfate (SDS) and nonionic emulsifier, poly(oxy ethylene) nonyl phenyl ether with an average of 40 oxy ethylene units per molecule (NP-40). The rate of polymerization and the number of polymer particles produced both increased with increasing

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the amount of NP-40 initially charged, when NP-40 was used as the sole emulsifier. Interestingly, however, both the rate of polymerization and the number of polymer particles produced was found to decrease, when the amount of NP-40 added to the fixed amount of SDS is increased in the mixed emulsifier. On the contrary, they both increased when the amount of SDS added to the fixed amount of NP-40 is increased in the mixed emulsifier. The mixed emulsifier did not affect the number of the radicals per polymer particle at a certain number of polymer particles, but affected the number of polymer particles, thus the rate of polymerization.

Keywords: Emulsion polymerization, Mixed emulsifier, Number of polymer particles

INTRODUCTION

Polymer latex produced by emulsion polymerization of acrylates such as methyl methacrylate (MMA) and n-butyl acrylate is used for paints. Anionic emulsifier such as sodium dodecyl

sulfate (SDS) is widely used in industrial emulsion polymerization. However, polymer latex produced by emulsion polymerization with anionic emulsifier is not stable enough against addition of pigments. To increase colloidal stability of the latex, a mixture of nonionic emulsifiers, which stabilize particles by thermodynamically favored steric repulsion, and anionic emulsifiers, which stabilize particles with electrostatic repulsion, is often used in emulsion polymerization. The number of kinetic studies on emulsion polymerization using mixed anionic and nonionic emulsifiers is not so many. Chern et al. [1] and Lin et al. [2] studied the effect of a mixed emulsifiers system with a nonionic emulsifier poly(oxy ethylene) nonyl phenyl ether with an average of 40 oxy ethylene units per molecule (NP-40) and the anionic emulsifier SDS on particle formation in the emulsion polymerization of styrene at 80^{o}C, changing the molar ratio of SDS to NP-40 in the mixture, but with fixing the total molar concentration of the two emulsifiers constant. They found that an increase in the molar ratio of NP-40 caused a decrease in the number of the polymer particles formed. But, both effect of decrease in SDS concentration and effect of increase in NP-40 concentration were superimposed on their experimental results. Therefore, in this study, we examined the effect of increasing the concentration of one emulsifier in the mixed emulsifier on the number of polymer particles produced in the emulsion polymerization of MMA with keeping the concentration of the other emulsifier constant.

EXPERIMENTAL SECTION:

Materials

Water deionized by MilliQ labo ZDQ2100 (Millipore ltd.) was used in all experiments.

Methyl methacrylate monomer (MMA, Wako, Guaranteed Degree) was purified with the following method: it was washed with a saturated aqueous solution of sodium hydrogen sulfite 3 times, with 5 wt% sodium hydroxide / 20 wt% sodium chloride aqueous solution 3times, and then with distilled water until pH of the waste water reaches around 7 (around 3 times). The washed monomer was distilled under vacuum (75mmHg) twice. The distilled MMA monomer was kept at –20 ^{o}C until use.

Nonionic emulsifier used in this study was poly(oxyethylene) nonyl phenyl ether with an average of 40 oxyethylene units (NP-40) (Sanyo Kasei Ltd.). Anionic emulsifier used was sodium dodecyl sulfate (SDS) (Nacalai tesque), a specially prepared grade for the detection of water-insoluble protein. Water-soluble initiator used is potassium persulfate (KPS) (Wako,

Guaranteed grade). NP-40, SDS and KPS were used without further purification.

Emulsion Polymerization Procedure and Characterization

Emulsion polymerization was carried out at 50 ^{o}C in a reactor with the same dimension as that used previously [3]. The recipe employed were: water 300g, methyl methacrylate monomer 0.2g/cc-water, KPS 1.25g/dm^3-water, and required amount of SDS and NP-40. At every certain reaction time, samples were withdrawn from the reactor for measurements of monomer conversion and particle number characterizations. Monomer conversion was measured gravimetrically with methanol (containing dilute hydrogen chloride) as precipitant. Volume-average particle size was measured with a transmission electron microscope (TEM). The number of polymer particles produced was calculated by using the obtained average particle size and monomer conversion.

RESULTS AND DISCUSSION

Effect of concentration of NP-40 in emulsion polymerization with NP-40

The emulsion polymerization of MMA was conducted with various concentration of NP-40. The obtained time-conversion curves are shown in Figure 1. For all systems, conversion increases almost linearly with time over conversion range from 10% to 30-40%. At higher conversion around 70 %, the rate of polymerization R_P increases slightly, which may be due to the so-called gel effect [4]. In the emulsion polymerization of methyl methacrylate with SDS as emulsifier, the monomer droplet is disappeared at around 30 % conversion [5]. The gel effect may take place at conversion higher than 30%. Furthermore, the concentration of monomer in the polymer particles, which affects the rate of polymerization, decreases after the monomer droplets disappear. Therefore, the rate of polymerization at conversion below 30% is mainly dealt with in this study. The rate of polymerization increased with concentration of NP-40.

The increase in the number of polymer particles produced usually increases the rate of polymerization. Thus, the numbers of polymer particles (N_T) produced in these systems were measured by TEM. The representative TEM image of the particles prepared with 30g/

dm^3-water NP-40 is shown in Figure 2(a). The particles are spherical and the surfaces of the particles are relatively smooth. So, the average diameter of polymer particles can be well measured from the TEM image. The numbers of polymer particles measured with TEM images are plotted against conversion in Figure 3. From Figure 3, the experimental error of the number of polymer particles measured with TEM is considered to be about twice. The number of polymer particles produced in each experiment increased with monomer conversion until monomer conversion reached 20%, and at higher conversion than 30% they became constant. The number of polymer particles increased by the increase in the concentration of NP-40.

In emulsion polymerization of MMA with SDS as a sole emulsifier, both the rate of polymerization and the number of polymer particles were reported to increase by the increase in the concentration of SDS [5]. Thus, both the rate of polymerization and the number of polymer particles increased by the increase in concentration of emulsifier in both emulsion polymerization with SDS as a sole emulsifier and that with NP-40 as a sole emulsifier.

For comparison between NP-40 and SDS, the time-conversion curve, the representative TEM image, and the number of polymer particles obtained by emulsion polymerization with SDS 8 g/dm^3-water as a sole emulsifier is shown in Figures 1, 2(b) and 3, respectively. The rate of polymerization with SDS 8 g/dm^3-water is similar to that with NP-40 30 g/dm^3-water.

As is clear from Figs. 2(a) and (b), the particles in both systems are spherical and their surfaces are relatively smooth. The number of polymer particles produced with SDS 8 g/dm^3-water is also similar to that with NP-40 30 g/dm^3-water. These results suggest that 30 g/dm^3-water NP-40 has similar effect on generation and stabilization of polymer particles as 8 g/dm^3-water SDS.

Effect of increase in NP-40 concentration at a constant concentration of SDS

The emulsion polymerization of MMA was conducted with fixed concentration of SDS; 8g/dm^3-water and changing the added amount of NP-40. The obtained time-conversion curves are shown in Figure 4. Addition of NP-40 so as to be 7.5g/dm^3-water decreased the rate of polymerization slightly. And addition of NP-40 so as to be no less than 15 or 30 g/dm^3-water did not changed the rate of polymerization, although the rate of polymerization with 30 g/dm^3-water NP-40 without SDS was similar to that with 8g/dm^3-water SDS without NP-40. The representative TEM image of the particles prepared with NP-40 7.5g/ dm^3-water and SDS 8g/dm^3-water is shown in Figure 2(c), with comparison of that with SDS 8g//dm^3-water shown in Figure 2(b). As is clear from Figure 2, the particles in both systems are spherical and

their surfaces are smooth. The average diameter of the particles obtained with the mixed emulsifier is larger than that with SDS as a sole emulsifier. The numbers of polymer particles (N_T) produced in these systems are plotted against conversion in Figure 5. The number of polymer particles decreased by addition of NP-40 so as to be 7.5 or 15 g/dm^3-water. These are unexpected results because the increase in NP-40 concentration increased both the rate of polymerization and the number of polymer particles produced. The addition of NP-40 into SDS causes the decrease in the rate of polymerization and the decrease in the number of polymer particles.

Effect of increase in SDS concentration at a constant concentration of NP-40

On the contrary to the experiments dealt with the former section, the emulsion polymerization of MMA was conducted with fixed concentration of NP-40; 7.5 g/dm^3-water and changing the added amount of SDS. The obtained time-conversion curve and the number of the polymer particles produced are shown in Figures 6 and 7, respectively. Both the rate of polymerization and the number of polymer particles increased with SDS concentration. These effects of addition of SDS are completely different from those of NP-40.

Discussion on the kinetics

It seems to be strange that the addition of NP-40 into emulsion polymerization with SDS decreased the rate of polymerization although the increase in NP-40 concentration increased the rate of polymerization in emulsion polymerization without SDS. In emulsion polymerization, the rate of polymerization is decreased by the decrease in average number of radicals per particle. The average number of radicals per particles is decreased by the increase in desorption of radicals from the particles [6], which may be increased by the desorption of radicals generated by chain transfer reaction to NP-40. So, the average number of radicals per particle in the emulsion polymerization with mixed emulsifiers is examined. If bimolecular termination in the aqueous phase is negligible (as is often with emulsion polymerization), average number of radicals per particle $\bar{n}$ can be expressed approximately as [7]:

$$\bar{n} = \frac{1}{2}\left[\left\{\left(\alpha_{\mathrm{w}} + \frac{\alpha_{\mathrm{w}}}{m}\right)^2 + 2\left(\alpha_{\mathrm{w}} + \frac{\alpha_{\mathrm{w}}}{m}\right)\right\}^{1/2} - \left(\alpha_{\mathrm{w}} + \frac{\alpha_{\mathrm{w}}}{m}\right)\right] + \left(\frac{1}{4} + \frac{\alpha_{\mathrm{w}}}{2}\right)^{1/2} - \frac{1}{2} \tag{1}$$

where the non-dimensional parameters, α_{w} and m are defined as follows.

$$\alpha_{\mathrm{w}} = \frac{r_{\mathrm{i}} V_{\mathrm{P}}}{k_{\mathrm{tP}} N_{\mathrm{T}}} \quad , \quad m = \frac{k_{\mathrm{f}} V_{\mathrm{P}}}{k_{\mathrm{tP}}} \tag{2}$$

where r_i is the rate of radical generation in the unit of molecules/cm^3-water.s, V_P is the average volume of a polymer particle, k_{tP} is the rate constant of bimolecular radical termination, k_f is the desorption rate coefficient of radicals from the polymer particles. The addition of NP-40 may change the value of k_f (so that the value of m) in the following 2 ways. 1) The radicals in the polymer particles may chain transfer to NP-40 molecules, which results in the generation of a new radical derived from NP-40. The generated radical may desorb out of polymer particles, which increases the value of k_f. 2) Adsorbed layer of NP-40 molecules on the surface of the polymer particles may retard the diffusion of a radical from the polymer particles, which decreases the value of k_f. On the other hand, the average number of radicals per particle $\bar{n}$ and α_w can be obtained experimentally from the rate of polymerization R_P given by:

$$R_P = k_P [M]_P \quad \bar{n} \quad N_T \tag{3}$$

where k_P is propagation rate constant, and $[M]_P$ is monomer concentration in polymer particles. The number of polymer particles produced in this study reached constant value at least monomer conversion 30%. Thus, the values of $\bar{n}$ and α_w at conversion 30% are calculated, respectively. The rate of polymerization R_P at conversion 30% is calculated from the slope of time-conversion curves. The radical generation rate r_i in Eq.(2) is expressed as:

$$r_i = 2\, k_d\, f\, [I]_0 \tag{4}$$

where k_d is initiator decomposition rate constant, f is initiator efficiency, and $[I]_0$ is the initial initiator concentration in the unit of molecules/cm^3-water.s. Figure 8 shows the values of $\bar{n}$ and α_w calculated by using Eqs.(2)-(4), and experimentally obtained values of N_T, R_P, V_P at monomer conversion 30% and using the values of constants listed in Table 1. In Fig.8, also plotted are the results of $\bar{n}$ obtained in the MMA emulsion polymerization with SDS as a emulsifier [5] and the values calculated with Eq.(1) by assuming the value of m being 0.04. The values of $\bar{n}$ and α_w in the emulsion polymerization with the mixed emulsifier system is on the same line of those with SDS alone, that is, on the line calculated by assuming the value of m being 0.04. This experimental finding means that the value of m with the mixed emulsifier system is almost same as those with SDS alone; 0.04. This suggests that the kinetics of the emulsion polymerization with the mixed emulsifier system is similar as that with SDS only, and hence, the desorption of radical generated by chain transfer to NP-40 is negligible, and the adsorbed layer of NP-40 on the surface does not retard the diffusion of a radical out of the particles significantly. So, the decrease in the rate of polymerization by the addition of NP-40 into emulsion polymerization with SDS is caused only by the decrease in the number of polymer particles.

The addition of NP-40 so as to be 15 g/dm^3-water did not change the rate of polymerization while it decreased the number of polymer particles produced, which seems to be apparently

contradicting results. This may be explained by the low dependency of the rate of polymerization on the number of polymer particles produced, in these emulsion polymerization conditions. The dependency of average number of radicals per particles $\bar{n}$ on the number of polymer particles produced is –5/6 when $\bar{n}$ is much less than a half [9]. The dependency of the rate of polymerization R_P on the number of polymer particles N_T is no more than 1/6 because in emulsion polymerization R_P can be expressed as Eq.(3). Thus, the decrease in the number of polymer particles did not decrease R_P so much.

The reason of the decrease in the number of polymer particles by addition of NP-40 into emulsion polymerization with SDS is still not clear. It was reported that hydrophilic polymer such as poly(vinyl pyrrolidone) adsorbs SDS molecules and generates a large micelle, and hence addition of such hydrophilic polymer decrease the number of micelles composed by SDS [10]. Addition of NP-40, which is a hydrophilic polymer, may decrease the number of the micelles and hence may decrease the number of the polymer particles produced, because the micelles are transformed into the polymer particles [11]. It was also reported that a large portion of NP-40 resides in the polymer particles [12]. The occlusion of NP-40 inside the polymer particles increases the volume of polymer particles, and hence increases the total surface area of the polymer particles and accordingly the number of SDS molecules adsorbed on the surface of the particles, which decreases the number of micelles left in the system.

Further study to clarify the reason is desired.

CONCLUSION

The effect of mixed emulsifiers (anionic SDS and nonionic NP-40) on the number of polymer particles produced in emulsion polymerization of methyl methacrylate was studied. With only NP-40, the number of the polymer particles increased with an increase in the concentration of NP-40. However, the number of polymer particles produced with 8g/ dm^3-water SDS and 7.5 or 15 g/ dm^3-water NP-40 is lower than that with 8g/ dm^3-water SDS without NP-40. The rate of polymerization does not increased by the addition of 7.5 or 15 g/ dm^3-water NP-40 into 8g/ dm^3-water SDS system. On the contrary, the number of polymer particles increased by addition of SDS into 7.5g/ dm^3-water NP-40 system. The reason of these results is not clear, although it was confirmed that the mixed emulsifier did not affect the number of the radicals per polymer particle at a certain number of polymer particles. Further study is desired to clarify the reason.

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Table 1 Values for constants used in calculation of $\bar{n}$ and α_w in emulsion polymerization of MMA at monomer conversion 30% and at 50 ^oC

Constant	Unit	Value	Reference
$[M]_P$	mol/dm^3	6.9	Nomura et al. [5]
k_P	$dm^3/mol.s$	648	Gilbert et al. [8]
k_{tP}	$cm^3/molecules.s$	$1.56x10^{-16}$	Nomura et al. [5]
$k_d f$	s^{-1}	$6.9x10^{-7}$	Nomura et al. [5]

Figure Captions

Fig.1 Time-conversion curves of emulsion polymerization with NP-40 without SDS compared with that with SDS 8g/dm^3-water

Fig.2 TEM images of the polymer particles produced at conversion around 0.8 in emulsion polymerization with (a) NP-40 30g/dm^3-water, (b) SDS 8g/dm^3-water, (c) NP-40 7.5g/dm^3-water and SDS 8g/dm^3-water.

Fig.3 The number of polymer particles produced in emulsion polymerization with NP-40 without SDS compared with that with SDS 8g/dm^3-water

Fig.4 Effect of addition of NP-40 into emulsion polymerization with 8g/dm^3-water SDS on time-conversion curves

Fig.5 Effect of addition of NP-40 into emulsion polymerization with 8g/dm^3-water SDS on

the number of polymer particles

Fig.6 Effect of addition of SDS into emulsion polymerization with 7.5g/dm^3-water NP-40 on time-conversion curves

Fig.7 Effect of addition of SDS into emulsion polymerization with 7.5g/dm^3-water NP-40 on the number of polymer particles

Fig.8 Relationship between average number of radicals per particle $\bar{n}$ and dimensionless parameter α_w

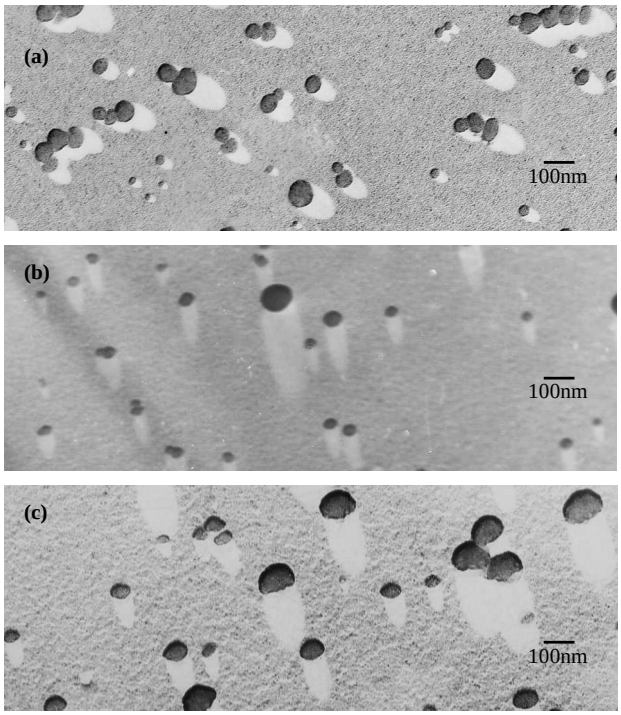

Fig.2 TEM images of the polymer particles produced at conversion around 0.8 in emulsion polymerization with (a) NP-40 30g/dm^3-water, (b) SDS 8g/dm^3-water, (c) NP-40 7.5g/dm^3-water and SDS 8g/dm^3-water.

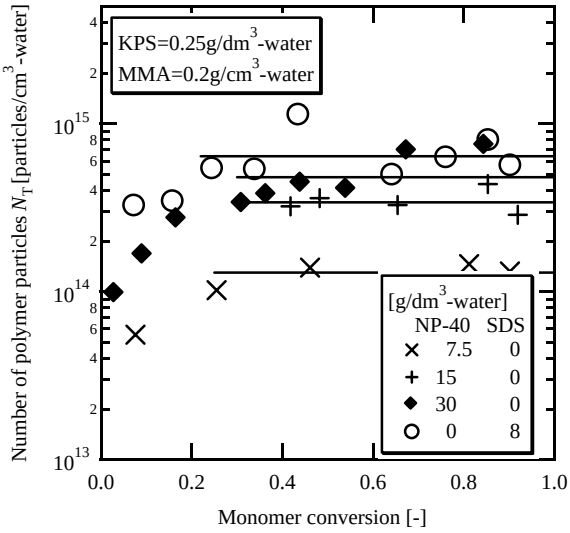

Fig.3 The number of polymer particles produced in emulsion polymerization with NP-40 without SDS compared with that with SDS 8g/dm^3-water

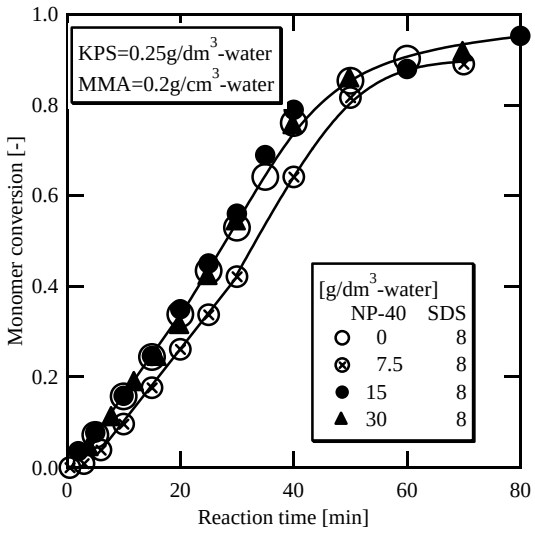

Fig.4 Effect of addition of NP-40 into emulsion polymerization with 8g/dm^3-water SDS on time-conversion curves

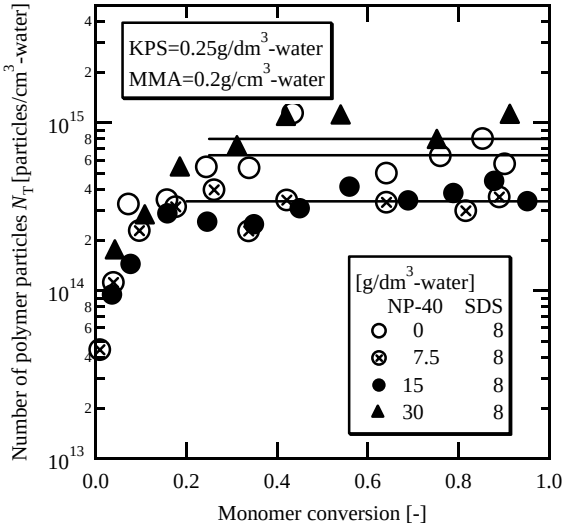

Fig.5 Effect of addition of NP-40 into emulsion polymerization with 8g/dm^3-water SDS on the number of polymer particles

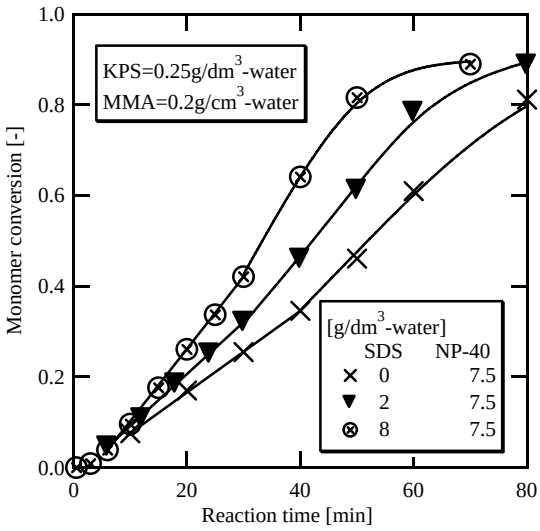

Fig.6 Effect of addition of SDS into emulsion polymerization with 7.5g/dm^3-water NP-40 on time-conversion curves

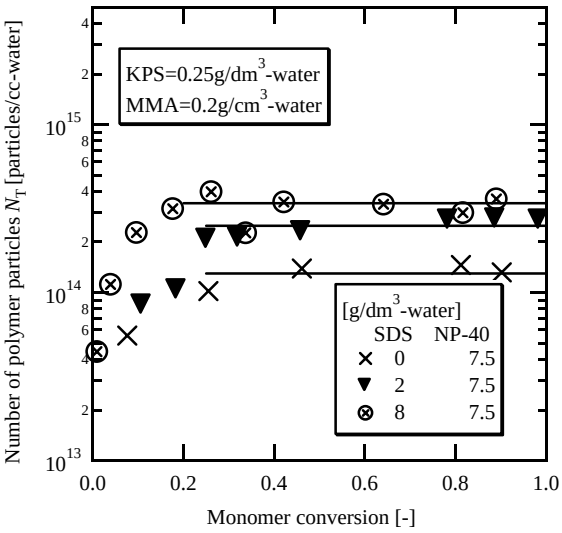

Fig.7 Effect of addition of SDS into emulsion polymerization with 7.5g/dm^3-water NP-40 on the number of polymer particles

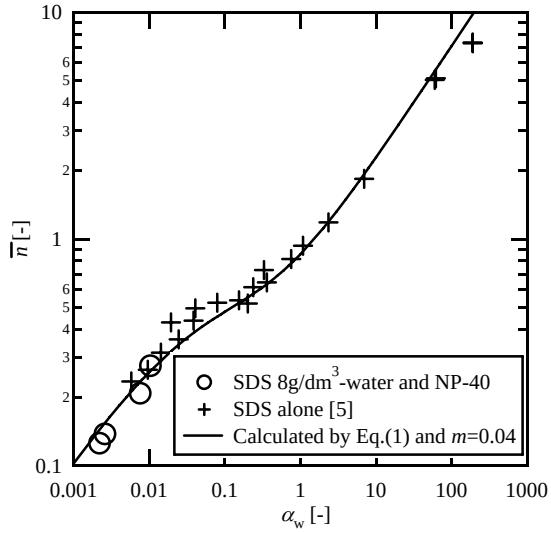

Fig.8 Relationship between average number of radicals per particle $\bar{n}$ and dimensionless parameter α_w